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Hydraulic cement-type fillers for hydrothermally stable polymer concretes

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Hydraulic cement fillers, which can prevent the hydrothermal decomposition of vinyl-type polymer concrete (PC) containing carboxylate groups in the polymer molecule, have been developed. Experiments were performed in which a co-polymer was used in combination with an aggregate containing various commercial cements such as Portland type I, III, and V cements, slag cement (IS), and a Class H oil-well cement. It was observed for Class H cement-filled PC that a strong interaction occurred between the cement grains and the CH_2 groups in the main chain of the co-polymer. The other cements exhibited lesser interactions. It was observed that after exposure to a 25% brine at 240° C, ionic bonding of carboxylate anions in the co-polymer with Ca^{2+} ions from the Class H cement and the hydration products of Class H cement had a significant effect on the strength. This improvement is believed to result from a reductive effect on the molecular mobility of the co-polymer chains. Fillers having a β-dicalcium silicate (C_2S)/Class H cement ratio from 0.7 to 1.5 made the greatest contribution to the hydrothermal stability of the vinyl-type PCs.

1. Introduction

It has been demonstrated that tricalcium silicate (C_3S) and dicalcium silicate (C_2S), the major chemical constituents of anhydrous cements, significantly affect the thermal stability and the physical properties of vinyl-type polymer concretes (PC) during exposure to hydrothermal conditions [1–3]. It was concluded that the effects are due to an interaction between the CH_2 groups in the main chain of the vinyl-type polymers and the $CaO–SiO_2$ (abbreviated form C–S) compounds in the cement. This results in ionic bonding between the Ca^{2+} ions of C–S compounds and the carboxylate anion ($-COO^-$) of polymers having carboxylate groups produced by hydrothermal degradation and the hydration products of C–S compounds.

In an evaluation of PCs as potential construction materials for use in geothermal processes, a general commercial type III Portland cement having a total C_3S and C_2S content above approximately 70% was used as a filler material. The cement content in the PC was varied from 10 to 50%. Results from field and laboratory tests at temperatures ranging from 90 to 240° C indicated that the composites containing the cement had far greater durability than samples containing fillers such as silica flour, calcium carbonate, and calcium hydroxide [1, 2].

On the basis of these observations, it was decided to perform a detailed evaluation of the effects of other commercially available cements such as types I, V, IS, Class H, and alumina. The evaluations were performed using differential thermal analysis (DTA), thermogravimetric analysis (TGA), infra-red spectroscopy, X-ray diffraction and physical property tests. In addition, a new type of cement having a more significant effect on the thermal stability of PC than commercial cement was prepared by the addition of β-C_2S with Class H cement.

2. Materials

A mixture of vinyl-type monomers consisting of 55 wt % styrene (St), 36 wt % acrylonitrile (ACN), and 9 wt % trimethylolpropane trimethacrylate

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TABLE I Chemical constituents of cement used as a filler of PC

Type and class of cement	Chemical constituents (%)							Specific surface* (cm^{2}g^{-1})
	CaO	SiO$_2$	Al$_2$O$_3$	MgO	Fe$_2$O$_3$	SO$_3$	Loss on ignition	
Type I	64.03	20.05	6.09	3.03	2.35	2.82	0.92	3350
Type III	63.77	19.82	2.37	3.10	2.37	3.27	0.86	4920
Type V	64.40	23.40	3.40	1.60	3.45	1.90	1.40	3800
Type IS	55.30	24.30	7.44	5.20	2.08	2.70	1.90	5225
Class H	64.40	22.10	4.00	1.00	4.48	2.70	0.50	2778
Alumina cement	37.86	6.70	39.52	1.65	9.84	1.10	0.78	–
Fly Ash	7.24	42.50	22.50	4.30	10.83	3.20	–	–

*Specific surface obtained from determination of the air permeability as measured using the Blain method.

(TMPTMA) was used in this study to produce a co-polymer upon polymerization. Polymerization was initiated by the use of 2 wt % benzoyl peroxide of 98% purity with subsequent heating at 85° C for 24 h.

The anhydrous cements used as filler materials in the PC were general commercial grade type I, III, V, IS, Class H, and alumina cements. Their chemical constituents and specific surfaces are given in Table I. For purposes of comparison with these various cement fillers, anhydrous gypsum plaster ($CaSO_4$) and fly ash were also evaluated as alternate filler materials.

The β-C_2S fillers containing a 0.6% free lime concentration were synthesized in the laboratory by heating mixtures of pure calcium carbonate and silica gel at 1350° C and subsequently grinding to a particle size of $< 62\,\mu$m. The aggregate used in the preparation of the PC was commercial silica sand having a particle size of 1.19 to 0.149 mm.

PCs were prepared by thoroughly mixing the dry ingredients by hand for ~ 2 min, and then adding the catalysed monomer and mixing for another 2 min.

3. Test methods

The differential thermal analysis measurements were performed using a DuPont 910 differential thermal analyser at a heating rate of 10° C min^{-1} in nitrogen gas. The DTA samples weighing 5 to 15 mg were crushed to a size to pass through a 0.104 mm sieve. Samples were evaluated before and after exposure for 10 days to 25% brine at 240° C.

The thermogravimetric analysis measurements were performed using a DuPont Model 951 TGA at a heating rate of 10° C min^{-1}. Samples, evaluated before and after exposure to hot brine, weighed from 15 to 20 mg and were crushed to a size < 0.104 mm. All tests were performed in nitrogen gas flowing at a rate of 80 ml min^{-1}.

A Perkin-Elmer Model 257 Spectrometer was used for infra-red analysis. The tests were performed by preparing KBr discs made by mixing 200 mg KBr and 3 to 5 mg PC which had been crushed to < 0.104 mm. The spectra were run at an 8 min scanning rate over the range of 4000 to 600 cm^{-1}.

Compressive strength tests were performed on duplicate samples before and after exposure to a hot brine solution for 10 days at 240° C. Specimens 2.2 cm in diameter and 4.4 cm long were used for compressive strength tests. Values were averages for three or two specimens.

4. Results and discussion

4.1. Thermal behaviour analysis

On the basis of the TGA thermograms of samples after exposure to hot brine, the effects of the various cements described above were determined. The weight losses of the co-polymers at 400, 450, and 500° C were obtained from isothermal TGA curves. These results are presented in Fig. 1. The weight loss of various cement-filled co-polymer systems occurring at 400° C were in the range of 8 to 13%. From these measurements, it appears that the amount of weight loss of co-polymer at temperatures above 450° C depends on the type of cement used. Samples containing Class H cement exhibited the smallest weight losses over the range of 400 to 500° C. At 450 and 500° C, the losses were about 27% and 75%, respectively.

TGA and DTA thermograms of co-polymer combined with Class H cement are illustrated in Fig. 2. The TGA curve for the co-polymer sample after exposure to hot brine indicates that the

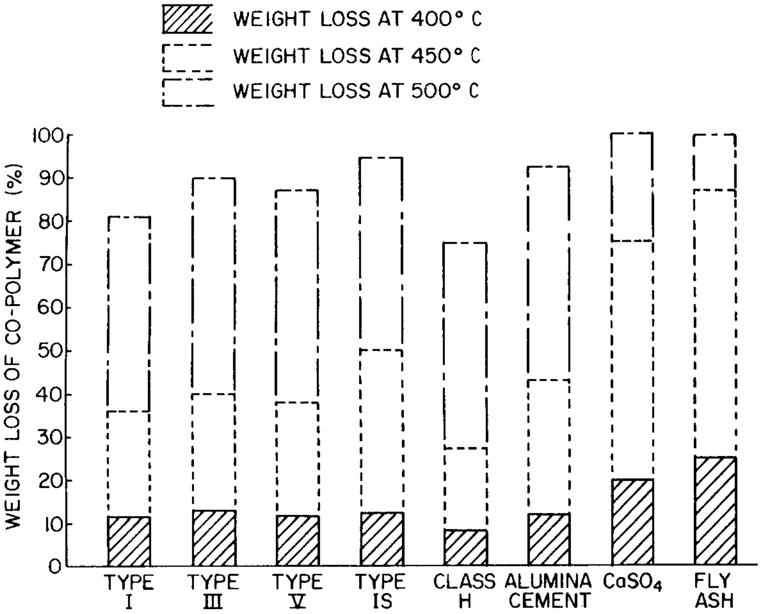

Figure 1 Weight loss obtained from TGA thermograms based on co-polymer contents of co-polymer-filled systems after exposure to 25% brine at 240° C for 10 days.

weight loss begins to occur slowly at approximately 300° C, and continues to occur at a reduced rate at temperatures above 500° C.

The TGA curve of the control samples shows no weight loss near 500° C because all of the polymer (34 wt %) in the samples had been completely decomposed at temperatures above 450° C.

The large exothermic peaks which serve to indicate the thermal decomposition of the co-polymer in the PC before and after exposure to hot brine, measured by DTA thermograms, were found to be in the temperature range of 395 to 465° C. The DTA thermogram of the sample after exposure to hot brine, showed an exothermic peak at 465° C

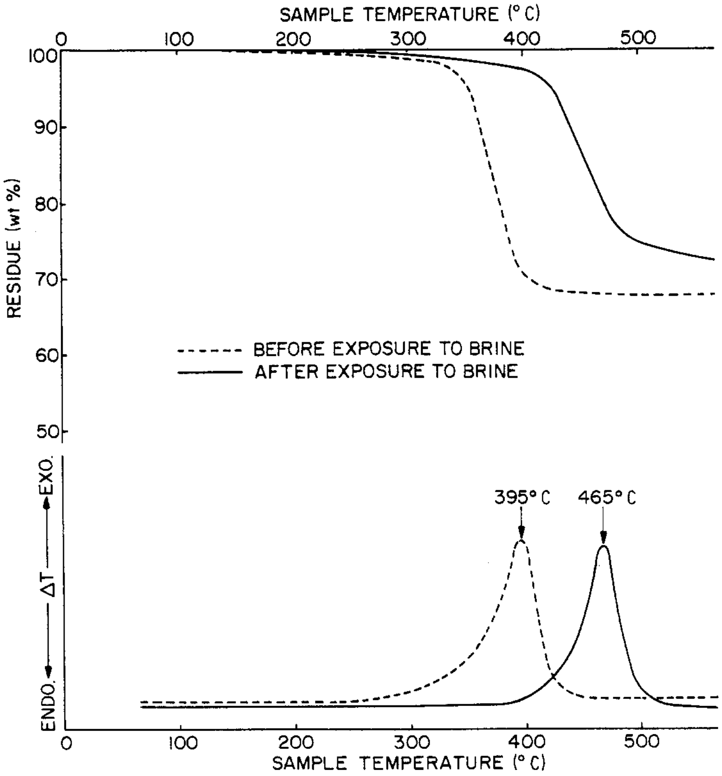

Figure 2 TGA and DTA curves of Class H cement-filled co-polymer before and after exposure to 25% brine at 240° C for 10 days.

compared to the 395° C value of the control sample.

These observations are considered to be due to the hydration products of Class H cement changing the co-polymer to a new molecular structure having thermal stability which surpasses that of the original molecular structure.

As shown in Fig. 1, type I, III, and V cements also affected the thermal stability but not to the extent of the Class H. The weight losses of co-polymer at 450 and 500° C for samples containing these cements were similar. Greater losses were exhibited by the samples containing the Type IS and alumina cements.

The TGA thermograms for $CaSO_4$ and fly ash-filled co-polymer samples after exposure to hot brine indicated a weight decrease of co-polymer of above about 20% at 400° C, above about 70% at 450° C, and 100% at 500° C. Silica flour-filled samples when exposed to identical conditions showed greater weight losses than $CaSO_4$ [1, 2].

The results of this analysis suggest that a new molecular structure is produced by the hydrothermal reaction occurring at the interface between the co-polymer and the hydraulic cement. The cement hydration products formed during exposure to the hydrothermal environment have a greater effect on the thermal stability of the co-polymer than do the unhydrated materials. It also appears that of the various cements used in this study, Class H enhances the thermal stability to the greatest degree.

4.2. Infra-red study

Infra-red analyses to study possible reaction mechanisms between C–S compounds and polymers before and after exposure to hot brine were reported in an earlier paper [3]. For polymer–calcium–silica samples before exposure to brine, an interaction between the C–S compounds and the CH_2 group in the main chains of vinyl-type polymers was confirmed by a reduction of the infra-red peak absorbance of CH_2 groups in the 3020 to 2900 cm^{-1} region. In addition, new peaks at 1540 and 1398 cm^{-1} indicated ionic bonding of Ca^{2+} ions of C–S compounds with the carboxylate anion ($-COO^-$) formed by the hydrothermal conditions.

On the basis of these experimental results, the degree of interaction occurring between the main chain of vinyl-type polymers and the various cements before an autoclave exposure, was evaluated from the experimental results obtained by calculating the absorbance ratio between the CH_2 groups at $\sim 2940\,cm^{-1}$ and the C=O groups at $1730\,cm^{-1}$. Furthermore, samples exposed in the autoclave were evaluated to determine the degree of ionic bonding between Ca^{2+} ions and the two carboxylate anions (COO^-). This was estimated from the absorbance at $1540\,cm^{-1}$ which is due to an asymmetric stretching vibration of the COO^- (Ca) groups. The effect of hydration products of the various cements produced during exposure to the autoclave, on the restraint of the thermal mobility of CH_2 groups in the main chain of co-polymer, were also considered with respect to the change in absorbance of CH_2 groups at $2940\,cm^{-1}$ before and after exposure to brine.

Results from the above studies are presented in Table II. As shown, the lower absorbance of CH_2 groups was less than $\sim 0.3 \times 10^{-1}$ and the absorbance ratio of co-polymer–cement–type composites less than ~ 0.76. When compared with that of the bulk co-polymer samples before exposure to hot brine, this suggests that there is a strong interaction between the main chain and the cement. Also, the lowest values of both the absorbance of CH_2 groups and the absorbance ratio indicate that the chemical affinity of Class H cement for CH_2 groups is stronger than for other types of cement.

The relationship between the specific surface of cement and the absorbance ratio is shown in Fig. 3. One of the reasons for the strong chemical affinity with Class H cement is the low specific surface of this type of material. A cement having a low specific surface has a stronger interaction with the CH_2 groups in the main chain than one having a high specific surface. In the cements used in this study, Class H cement has the lowest specific surface with a value of $2779\,cm^2\,g^{-1}$. Possible interactions of cements having a specific surface under $2778\,cm^2\,g^{-1}$ with CH_2 groups were not investigated in this study.

Ca^{2+} ions produced from the cement in an aqueous medium develop an electrostatic interaction with the carboxylate groups ($-C{=}O^{-\delta}$) in the TMPTMA molecule used as a cross-linking agent in the co-polymer. These groups are made more strongly electropositive by the elevated temperature. Thus, the carboxylate group can be easily changed to the carboxylate anion ($-COO^-$) by the electrostatic interaction. Ca^{2+} ions may be present to perform a cross-linking function which connects two $-COO^-$ groups between co-polymer chains and within a single chain [4–6].

TABLE II Infra-red absorbance analysis of co-polymer-filled systems before and after exposure for 10 days to 25% brine at 240° C

Composition	Before exposure to brine		After exposure to brine	
	Absorbance of CH_2 $\left(\frac{2940\ \text{cm}^{-1}\ \text{of}\ CH_2}{\text{mg in disc}}\right) \times 10^{-1}$	Absorbance ratio $\left(\frac{2940\ \text{cm}^{-1}\ \text{of}\ CH_2}{1710\ \text{cm}^{-1}\ \text{of}\ C{=}O}\right)$	Absorbance of CH_2 $\left(\frac{2940\ \text{cm}^{-1}}{\text{mg in disc}}\right) \times 10^{-1}$	Absorbance of $-COO^-(Ca)$ $\left(\frac{1540\ \text{cm}^{-1}}{\text{mg in disc}}\right) \times 10^{-1}$
100% P*	0.66	0.813	0.99	–
34% P–66% type I	0.19	0.522	0.22	0.79
34% P–66% type III	0.20	0.547	0.24	0.77
34% P–66% type V	0.17	0.528	0.20	0.79
34% P–66% type IS	0.24	0.610	0.27	0.58
34% P–66% Class H	0.14	0.507	0.17	0.75
34% P–66% alumina cement	0.25	0.604	0.28	0.61
34% P–66% fly ash	0.38	0.725	0.54	–
34% P–66% $CaSO_4$	0.32	0.764	0.32	0.81

*P = 55 wt% styrene–35 wt% acrylonitrile–9 wt% TMPTMA.

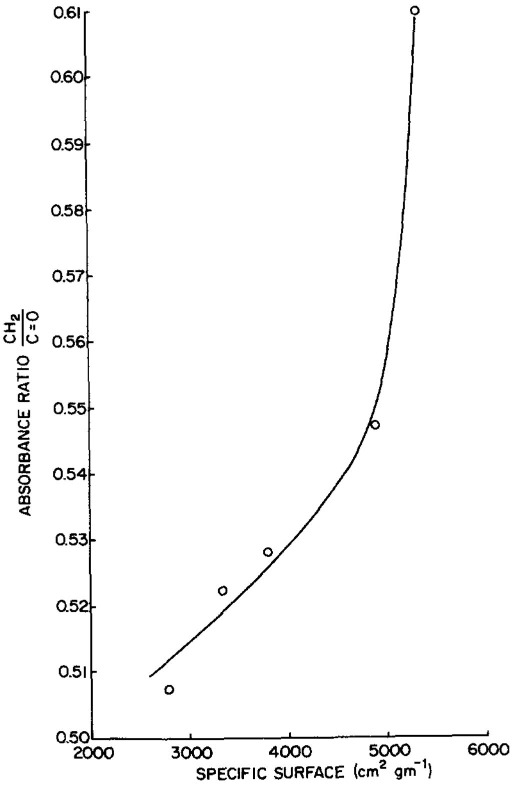

Figure 3 The effect of the specific surface of anhydrous cement on the absorbance of CH_2 and C=O groups.

The degree of ionic bonding for Ca–polymer complexes may be represented by the intensity of absorbance at 1540 cm^{-1}. The absorbance of —COO$^-$(Ca) groups at 1540 cm^{-1} in PC samples containing type I, III, V, or Class H cements showed values above 0.75, as indicated in Table II. This can be considered due to a direct effect of the CaO included as a chemical constituent of cement upon the intensity of the absorbance of the —COO$^-$(Ca) groups. Thus, if the chemical constituents of various cements indicated in Table I are considered, the CaO content necessary to form a cross-linking structure with two carboxylate anions (—COO$^-$) in a co-polymer molecule may be above 64%. The highest absorbance value, 0.81 x 10^{-1}, was obtained from CaSO$_4$-filled co-polymer samples. This is due to the greater amount of Ca^{2+} ions released by the rapid hydration reactions in an aqueous medium.

After exposure to a hydrothermal environment, the increase in absorbance of the CH_2 group of co-polymer–cement samples was < 20%. However, the absorbance increases of CH_2 groups for bulk co-polymer and fly ash-filled co-polymer samples were 50% and 42%, respectively. This difference is assumed to be due to a significant effect of the hydration products of cement on the restraint of the molecular mobility of the main chain caused by the attack of hot brine.

In order to clearly demonstrate the chemical reaction between the cement and the co-polymer that occurred during the autoclave exposure, the infra-red spectra of bulk co-polymer and Class H cement-filled co-polymer samples, before and after exposure to hot brine, are illustrated in Fig. 4.

Infra-red absorption bands of the 55 wt % styrene–36 wt % ACN–9 wt % TMPTMA co-polymer samples before exposure to brine (sample a in Fig. 4) indicate a symmetric stretching vibration of CH_2 groups at 2940 cm^{-1}, a stretching vibration of C=N groups at 2240 cm^{-1}, and a stretching vibration of C=O groups at 1710 cm^{-1}. The spectra for the co-polymer after exposure for 10 days to hot brine at 240° C (sample b) exhibited four new bands at ~ 3400, ~ 3200, ~ 1560, and ~ 1400 cm^{-1} in place of the nitrile group at 2240 cm^{-1}. The absorption bands at 3400 and 3200 cm^{-1} can probably be attributed to the amine groups. The 1560 cm^{-1} band is due to conjugated —(C=N)x^- groups [7–9]. The weak band at ~ 1400 cm^{-1} may be due to a symmetric vibration of carboxylate anions (—COO$^-$) formed by the hydrothermal decomposition of some of the carboxylate groups in the TMPTMA molecules. It appears from the absorption band at ~ 1700 cm^{-1} that a majority of the C=O groups in TMPTMA are not affected by hot brine.

The infra-red spectra of Class H cement-filled co-polymer samples after exposure to hot brine (sample d in Fig. 4) is characterized by two prominent absorption bands occurring around 1540 and 1400 cm^{-1}. These bands are attributed to asymmetric and symmetric stretching vibrations of the COO$^-$(Ca) group, which may be due to ionic bonding occurring between Ca^{2+} ions and carboxylate anions (COO$^-$). The COO$^-$(Ca) group produced during hydrothermal exposure can also be detected by the disappearance at 1710 cm^{-1} of the C=O group band which was present in the samples before exposure (sample c). The band of conjugated —(C=N)x-groups at 1500 cm^{-1} seems to be marked by a large band at 1540 cm^{-1}. These infra-red absorption bands suggests that the production of Ca–polymer complexes is due to the presence of Ca compound fillers which can be converted

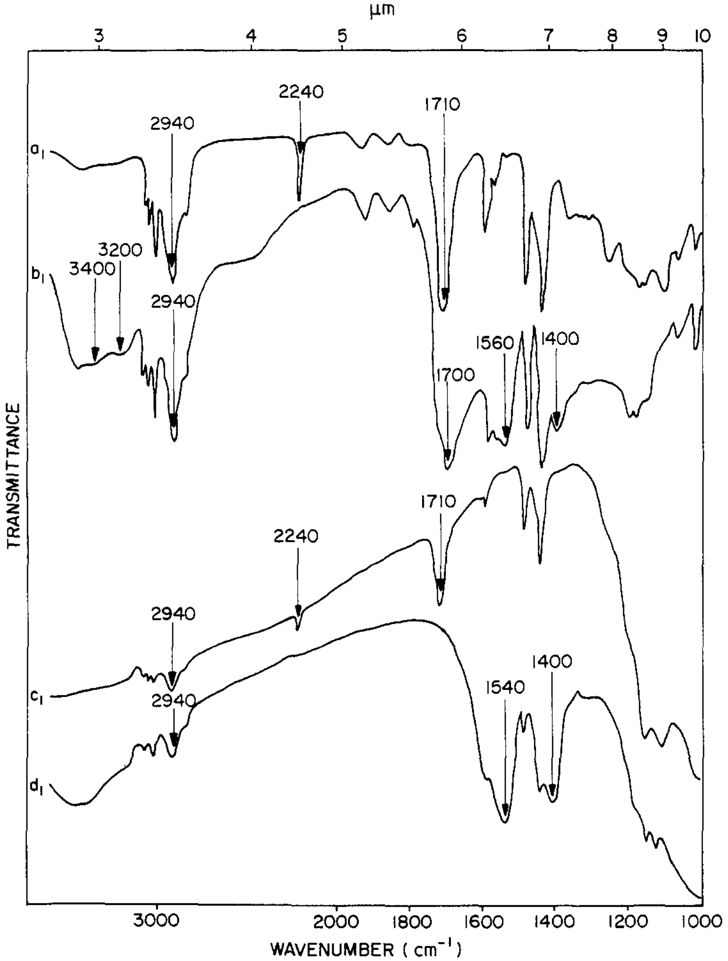

Figure 4 Infra-red spectra of copolymer-Class H cement systems before and after exposure to hot brine.

easily to the Ca^{2+} ions by an aqueous medium at elevated temperature. The Ca^{2+} effect can be explained by the following equation which indicates the general configuration of polymer chains in an aqueous medium as described by Kuhn and Kuhn [10].

$$Q = \frac{L_{\max}}{r^{-2}}$$

where Q is the rate of coiling into a ball which is caused by active segmental motion of polymer chains in a solution, $L_{\max}$ the total length of a single chain, and r^{-2} the average obtained by squaring the distance between the chain ends. This equation shows that the rate of polymer coiling decreases with a lengthening of the distance between chain ends.

Using the above equation, it is very interesting to consider how Ca^{2+} ions produced by hydrothermal conditions can restrain a molecular coil of polymer chains. For the restraining of segmented motion due to ionic bonding, the Ca^{2+} having a larger radius of 0.99 Å may increase the distance between two $-COO^-$ anions. It can be assumed that this bonding may increase the value of r^{-2} in the equation, and this effect may restrain the polymer chains from coiling into a ball. Also, it is possible that the hydration products of the cement filler have a sufficient restrictive effect against the moving polymer chain segments that occur in an aqueous medium at elevated temperature.

From the results of thermal behaviour and infra-red studies described above, it appears that significant improvement in the hydrothermal stability of vinyl-type polymer concretes having carboxylate groups in their polymer molecules can be obtained by using fillers containing compounds having a specific surface under ~ 3000 cm^2 g^{-1}, CaO as a main ingredient, and the ability to easily form a hydration product upon reaction with hot brine.

TABLE III Compressive strength and X-ray intensity of cement mortar specimens cured under water for 7 days before and after exposure for 10 days in an autoclave at 240° C

Type and class of cement mortar*	Compressive strength (psi) (MPa)†		Difference, (%)	X-ray intensity‡ at 3.07 Å
	Before autoclave	After autoclave		
Type I	5174 (35.7)	3353 (23.1)	− 35.2	5
Type III	5321 (36.7)	3734 (25.7)	− 29.8	7
Type V	3323 (22.9)	2539 (17.5)	− 23.5	9
Type IS	5020 (34.6)	3373 (23.2)	− 32.8	3
Class H	2346 (16.2)	2713 (18.7)	+ 15.6	24
Alumina cement	3241 (22.3)	2451 (16.9)	− 24.4	§

*All cement mortar specimens prepared with a water to cement ratio of 0.39 and a cement to sand ratio of 0.61.

†Values are averages for two 2.2 cm diamter × 4.4 cm long cylindrical specimens.

‡Intensity of the xonotlite crystal at 3.07 Å of samples after exposure in an autoclave.

§Peak at 3.07 Å did not appear.

4.3. Physical properties

In a previous paper, it was shown that one of the important factors determining the physical properties of polymer–cement PCs upon exposure to hot brine is the formation of cement hydration products [2, 11]. Therefore, tests to estimate the thermal stability of the materials during long-term exposure to hydrothermal environments were undertaken.

Compressive strength and X-ray diffraction tests were performed. In the latter, the intensity of xonotlite crystals at 3.07 Å of various cement mortar specimens prepared by using a water-to-cement ratio of 0.39 and a cement-to-sand ratio of 0.61 was determined. It is well known that xonotlite (C_6S_6H) produced by the reaction of CaO with SiO_2 in an autoclave at about 300° C has thermal stability and moderate strength at about 400° C [12]. These hydration products, therefore, have a significant effect on the long-term thermal stability at elevated temperatures.

The results, given in Table III, indicate that exposure to hot brine increases the compressive strength of Class H cement mortar specimens by about 16%. However, the compressive strength of other cement mortar specimens was reduced by more than 20%. The improvement in strength of Class H cement mortar specimens may be due to the xonotlite produced by the hydrothermal reaction occurring between the Class H cement and the silica sand. The X-ray intensity of xonotlite at 3.07 Å formed from Class H cement specimens is higher than for other types of cements. The results suggest that the long-term hydrothermal stability of Class H cement–silica and systems is due to the formation of xonotlite.

The initial compressive strengths and changes in strength after exposure for 10 days to 25% brine at 240° C are given in Figs. 5 and 6. Four PC formulations given below were evaluated.

12 wt % co-polymer – 84 wt % silica sand – 4 wt % cement

12 wt % co-polymer – 80 wt % silica sand – 8 wt % cement

12 wt % co-polymer – 70 wt % silica sand – 18 wt % cement

13 wt % co-polymer – 54 wt % silica sand – 33 wt % cement

The size and the mix proportions of the silica sand used in this study were 50 wt % no. 16 sand (size, 1.19 mm)–25 wt % no. 30 sand (size, 0.595 mm)–25 wt % no. 100 sand (size, 0.149 mm).

As shown in Fig. 5, the addition of less than about 10% cement produces no significant improvement in strength of PC, because of an inhomogeneous distribution of cement filler within the polymer. For PC specimens containing above 15% cement, the improvement in strength of specimens after exposure to hydrothermal conditions appeared to be dependent on the type of cement. The compressive strengths of PC specimens containing 18% type I, III, V, and Class H cements are in the region of 12 000 to 13 200 psi (82.7 to 91.0 MPa). However, the specimens combined with type IS and alumina cements indicate a lower strength, compared with those of the other specimens. The highest strength PC specimen after exposure to hot brine was a 34 wt % Class H cement-filled co-polymer PC. In contrast, PC specimens containing $CaSO_4$ and fly ash indicated far lower strengths than specimens containing the vari-

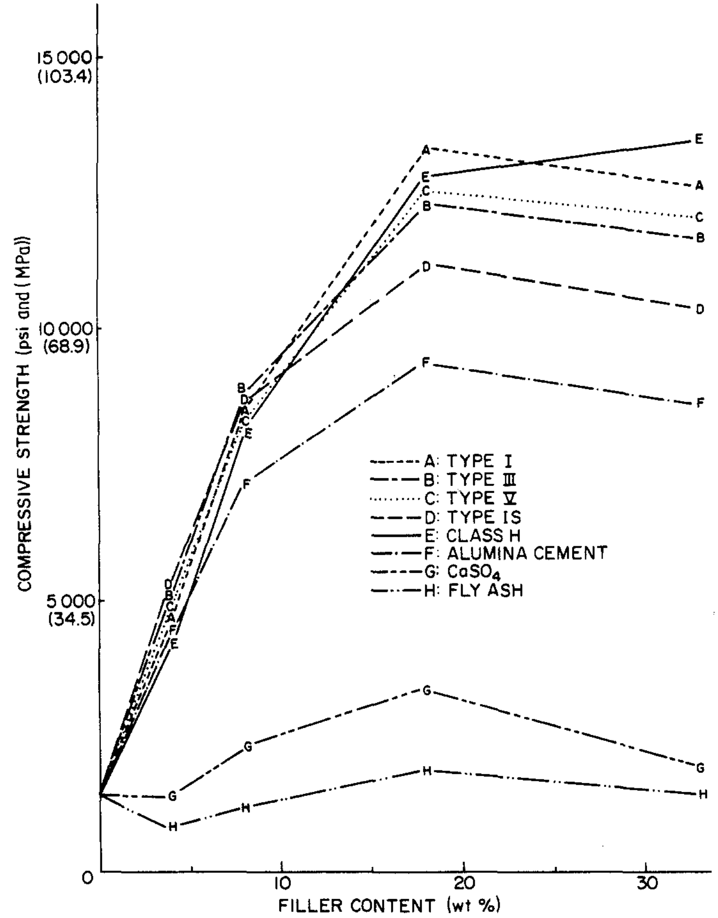

Figure 5 Compressive strength of PC specimens containing various fillers after exposure to 25% brine at 240° C for 10 days.

ous cements. This seems to demonstrate that $CaSO_4$ and fly ash fillers do not contribute significantly to the improvement in compressive strength of PC after exposure to brine.

In order to understand further the effect of the various cements on the thermal stability of PC, the differences in compressive strength of the various cement-filled co-polymer PCs before and after exposure to hot brine are illusstrated in Fig. 6.

The data indicate that in comparison with control specimens, there is an ~ 18% increase in the strength of PC containing concentrations of type I, III, V, and Class H cements after exposure to hot brine. At 34% concentrations, Class H cement made the greatest contribution to the strength, which increased ~ 14%. The type I, III, and V cement-filled PC specimens all showed lesser increases in strength and the values were not significantly different from each other. PC specimens containing 4 to 33% alumina cement do not exhibit an increase in strength caused by production of hydration products and Ca–polymer complexes. The data also suggest that the strength of PC after exposure to hot brine increases with an increase in the concentration.

From the results of the physical property studies described above, API Class H cement from among the various types of cements used in this study can be identified as a filler having a significant effect on the hydrothermal stability of vinyl-type PCs which have carboxylate groups in their molecules. These effects are believed to be due to the calcium silicate hydrates formed in the hydration process and the Ca–polymer complexes formed during the autoclave exposure. The details on the calcium silicate hydrates produced in PC have not been published. However, X-ray diffraction analysis of β-C_2S-filled co-polymer PC after exposure for 30 days to 25% brine at 240° C, showed a characteristic sharp peak of C–S–H(I) at 3.06 Å. Thus, it can be assumed that the mixture of Class H cement and silica sand existing in PC also produces xonotlite after exposure for a long term in an autoclave at elevated temperature.

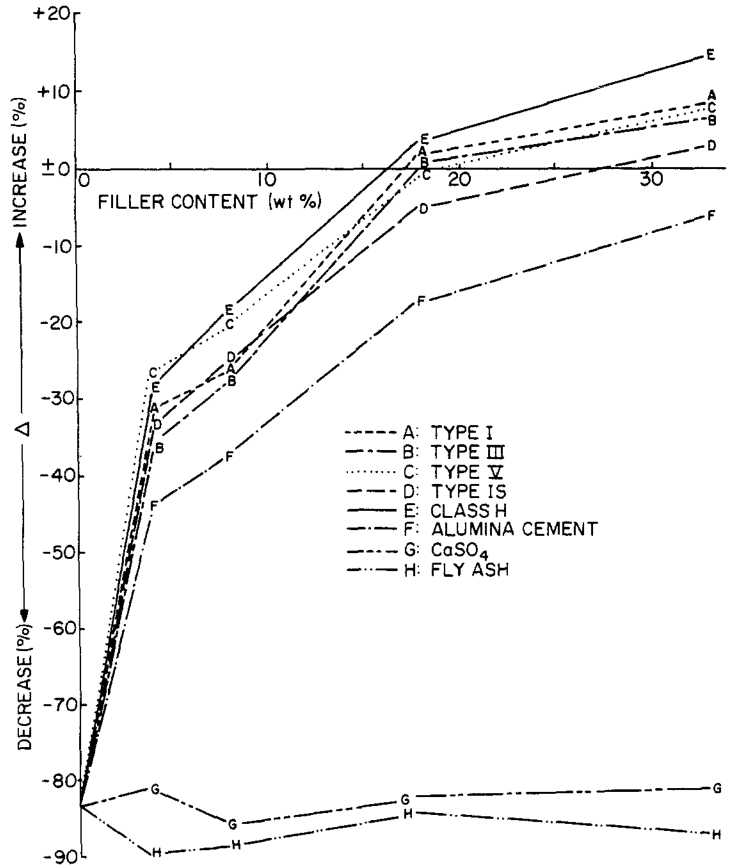

Figure 6 The difference in compressive strength of PC containing various fillers before and after exposure to hot brine at 240° C for 10 days.

4.4. Development of hydraulic cement-type filler

On the basis of the chemical constituents of Class H cements, adjustment of the chemical composition to yield a new type of cement which has a greater effect on the hydrothermal stability of PC than Class H cement was made. It was reported in previous papers [1, 2] that the use of C_3S and C_2S as additives to the inorganic phase significantly affects the thermal stability of PC. Therefore, a mixture of Class H cement and β-C_2S which easily forms xonotlite when compared with C_3S was evaluated.

The results obtained from this series of tests are shown in Table IV. The data indicate that the compressive strength of PC specimens is increased by replacement of the Class H cement with β-C_2S. The strength after exposure to brine of PC, in which all of its Class H cement was replaced by β-C_2S, was 15 213 psi (104.8 MPa). This strength is

TABLE IV Compressive strength and water absorption of PC containing Class H cement–β-C_2S system filler after autoclave exposure

Composition*	Water absorption† (wt%)	Compressive strength‡ (psi) (MPa)
11.4% P–70.9% S–17.7% Class H– 0.0% C_2S	1.07	12634 (87.1)
11.7% P–70.7% S–14.1% Class H– 3.5% C_2S	0.81	14 026 (96.6)
12.0% P–70.4% S–10.6% Class H– 7.0% C_2S	0.76	14 967 (103.1)
12.6% P–69.9% S– 7.0% Class H–10.5% C_2S	0.73	15 120 (104.2)
13.2% P–69.4% S– 3.5% Class H–13.9% C_2S	0.70	15 204 (104.8)
13.5% P–69.2% S– 0.0% Class H–17.3% C_2S	0.68	15 213 (104.8)

*P = 55 wt% styrene–36 wt% acrylonitrile–9 wt% TMPTMA: S = 50 wt% no. 16 sand (size, 1.19 mm)–25 wt% no. 30 sand (size, 0.595 mm)–25 wt% no. 100 sand (size, 0.149 mm); C_2S = β-C_2S.

†Water absorption in boiling water for 5 h.

‡Specimens, 2.2 cm diameter × 4.4 cm long cylinders. Values are averages for three specimens.

TABLE V The chemical compounds of cement obtained in this study

C_3S(%)	C_2S(%)	C_3A(%)	C_4AF(%)
30.8–20.5	55.1–70.0	1.6–1.1	8.6–5.8

In the abbreviated formula $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$; plus gypsum, lime, and alkali.

about 1.2 times greater than that of PC filled with Class H cement only.

The water absorption of PCs containing mixtures of β-C_2S and Class H cement exhibits a gradual decrease with an increase in the amount of β-C_2S substituted for Class H cement.

Because β-C_2S is a very expensive material (approximately ten times the cost of Class H cement), it is best used in a blend with Class H cement thereby keeping the cost to a minimum while still retaining the advantages that this material provides to a PC.

If the most suitable ratio of β-C_2S to Class H cement is estimated from the results of tests on compressive strength (see Table IV), a ratio in the region of 0.7 to 1.5 appears to be economically reasonable. The strength of this formulation would be only about 2.5% lower than one containing 100% β-C_2S.

The chemical compounds of this hydraulic cement-type filler having a β-C_2S/Class H cement ratio from 0.7 to 1.5, based upon calculation, are given in Table V.

5. Conclusions

The following generalizations can be given as characteristic conditions for anhydrous cement fillers which are necessary to prevent hydrothermal decomposition of PC produced using monomers containing carboxylate groups in their molecules.

(1) A specific surface under $3000\,cm^2\,g^{-1}$ is required to obtain a strong interaction with the CH_2 groups in the main chain of polymer.

(2) In order to produce an adequate amount of Ca^{2+} ions, which form an ionic bond with carboxylate anions ($-COO^-$) of the polymer in an aqueous medium at an elevated temperature, it seems to be necessary to have the CaO content of the filler above 64.0% when it is obtained as a chemical constituent of cement.

(3) The calcium silicate hydrates produced by the hydrothermal reaction between silica sand and C–S compounds during long-term autoclave exposure, have a significant effect on the hydrothermal stability of PC.

(4) Materials having a β-C_2S and Class H cement ratio from 0.7 to 1.5 were identified as fillers which would contribute significantly to the hydrothermal stability of vinyl-type PC.

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References

1. T. SUGAMA and L. E. KUKACKA, *J. Cement Concrete Res.* **9** (1979) 69.
2. T. SUGAMA, L. E. KUKACKA and W. HORN, *ibid* **9** (1979) 461.
3. *Idem. J. Appl. Polymer Sci.* **24** (1979) 2121.
4. I. MICHAELI, *J. Polymer Sci.* **48** (1960) 291.
5. J. C. LEYTE, L. H. ZUIDERWEG and H. J. VLEDDER, *Spectrochimica Acta* **23A** (1967) 1397.
6. S. CRISP, H. J. PROSSER and A. D. WILSON, *J. Mater. Sci.* **11** (1976) 36.
7. W. J. BURLANT and J. L. PARSONS, *J. Polymer Sci.* **22** (1956) 249.
8. N. GRASSIE and J. N. HAY, *ibid.* **56** (1962) 189.
9. W. N. TURNER and F. C. JOHNSON, *J. Appl. Polymer Sci.* **13** (1969) 2073.
10. W. KUHN and H. KUHN, *Helv. Chim. Acta* **26** (1943) 1394.
11. T. SUGAMA, L. E. KUKACKA and W. HORN, *Int. J. Cement Composities.* **2** (1979) 55.
12. G. L. KALOUSEK, Development of Cement For Geothermal Wells, Final Report, BNL 51024, March (1979).

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